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Perfluoroalkylpolyethers

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I. DEVELOPMENT

Perfluoroalkylpolyether (PFPE) fluids were first synthesized by DuPont. The first applications were military/aerospace in nature. Joint development efforts with the U.S. military and NASA led to greases that were developed to take advantage of the high temperature lubricating abilities of the oils. Gumprecht [1] first disclosed the use of the perfluoroalkylpolyethers as lubricants in a lubrication conference sponsored by the American Society of Lubricating Engineers and the American Society of Mechanical Engineers in the fall of 1965.

First applications took advantage of the chemical inertness, thermal stability, and nonflammability of the fluids. They are used for the following purposes:

- as valve and O-ring lubricants in oxygen service (because of their nonflammability and stability in oxygen atmospheres)
- as lubricants for aircraft instrument bearings (because of their low vapor pressure)
- as seal lubricants in reactive chemical environments (because of their chemical inertness, high temperature stability, and insolubility to chemicals)
- as sealed-for-life electric motor bearing greases (because of their good lubricity and because the oils do not oxidize and fail)
- as high temperature greases (because of their ability to withstand constant temperatures up to 550°F and intermittent temperatures up to 650°F or higher)

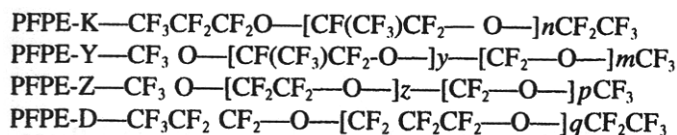
Additional applications include base oils for specialty greases, antiseize, instrument oils, chlorine and oxygen service lubricants, valve greases, and mechanical seal barrier fluids; lubricants in the nuclear industry and in many high temperature systems; and lubricants for conveyor bearings, textile and plastics tenter frames, and pressure relief valves. They lubricate rocket nozzles, automotive antilock braking systems, gold contacts, and sintered bearings. The largest current use for PFPE fluids is in vacuum pumps. They are specified by vacuum pump manufacturers as a high vacuum, nonflammable fluid that can be safely used with the reactive chemicals found in computer chip manufacture.

II. CHEMISTRY

Perfluoroalkylpolyether fluids are composed entirely of carbon, fluorine, and oxygen. They are colorless, odorless, completely inert to almost all chemical agents including oxygen, compatible with most other materials, and liquid over a wide temperature range.

A. Product Structures

Although all PFPE types exhibit similar physical and chemical properties, there are small and sometimes significant differences. Since the initial development, the following four distinct types of PFPE oil have become commercially available.



Both PFPE-K and PFPE-Y are nonlinear molecules, because the polymer chains contain pendant trifluoromethyl groups, (---CF_3). PFPE-D and PFPE-Z contain no pendant groups and are linear. The linear PFPE structures show less change of viscosity with temperature and pressure than do nonlinear PFPE.

Pendant trifluoromethyl groups immediately adjacent to the ether (---O---) linkage provide some shielding to protect that linkage from acid-catalyzed cleavage. PFPE-K has a fully shielded polymer chain, because every ether linkage is adjacent to a carbon with a pendant trifluoromethyl group. PFPE-Y has a partially shielded polymer chain, because less than half of all ether linkages are protected with a pendant trifluoromethyl group. PFPE-D and PFPE-Z have nonshielded polymer chains and are thus not protected from acid-catalyzed cleavage.

PFPE-K and PFPE-D contain one type of ether group and are homopolymers, while PFPE-Y and PFPE-Z contain ether groups of two types. PFPE-Y and PFPE-Z both contain the difluoroformyl ($\text{---CF}_2\text{O---}$) linkage as well as the perfluoropropyl or perfluoroethyl group, respectively. Even though PFPE-Y and PFPE-Z appear to be copolymers, they are prepared using only one monomer.

B. Preparation of PFPE Types

Perfluoroalkylpolyethers, PFPE-K, are prepared by anionic polymerization of hexafluoropropylene epoxide (HFPO) at low temperatures. The preparation of HFPO has been described [2,3]. HFPO can be polymerized in solvents such as aliphatic hydrocarbon polyethers or nitriles using cesium fluoride as the source of fluoride ions. The reaction temperature is -24°C , the boiling point of HFPO.

The intermediate polymer contains an acid fluoride end group that is much too reactive for use in lubricants. The polymer is stabilized [4] by reaction: first with water, forming the carboxylic acid, and then with elemental fluorine. The polymer as prepared has a molecular weight range of 435–13,500 and is then fractionated into different viscosity grades by vacuum distillation.

PFPE-Y is prepared by the photochemical-catalyzed polymerization of hexafluoropropylene in the presence of oxygen at low temperatures [5]. Treatment with UV light or heat or both causes decomposition of the peroxide linkages. End groups include either OCOF or CF_2COF and are removed by high temperature treatment with elemental fluorine, giving a polymer

containing two types of perfluoroalkyl linkage in the polymer chain: $[-OCF_2-]$ and $[-OCF(CF_3)CF_2-]$. The molecular weight range of this polymer is 1000–10,000. An excellent review is found in Ref. 6.

PFPE-Z is produced when tetrafluoroethylene is used as the starting material instead of hexafluoropropylene [7], and the crude polymer is processed just as with PFPE-Y. The PFPE-Z crude polymer has a higher molecular weight distribution than PFPE-Y, ranging from 8000 to 70,000. During the stabilization process, however, the molecular weight decreases because chains are cleaved into smaller pieces. The reaction mechanism and kinetic equation for the photooxidation of fluoroolefins to PFPE-Y and PFPE-Z is described by Sianesi et al. [8].

PFPE-D is obtained by Lewis acid catalyzed ring-opening polymerization reaction of 2,2,3,3-tetrafluorooxetane [6]. The hydrogen–carbon bonds are subsequently converted to fluorine–carbon bonds by direct fluorination with elemental fluorine. Ultraviolet light catalyzes the direct fluorination.

The crude polymers of all types are usually purified by contact with absorbing agents to remove polar materials, followed by distillation under reduced pressure. The reaction mass is fractionated by distillation into specific molecular weight and viscosity ranges. These ranges usually correspond to different grades or product types available commercially.

C. Functional Fluids and Soluble Additives

Conventional hydrocarbon-based additives do not dissolve in PFPEs because of the PFPEs' extreme inertness and insolubility in chemicals. Because of this, the oils have not been used in some applications calling for anticorrosion additives or extreme pressure additives. Solid additives have been added to greases because the thickener will hold them in place, but the additives cannot be used in oils.

A number of soluble anticorrosion and wear-reducing additives have been developed in the last few years to address the deficiencies of the oils. In addition to protecting the surfaces, these new products raise the temperature at which the oil decomposition reaction begins, allowing the fluids to be used at higher temperatures [9].

Functional fluids have been polymerized to handle specific applications and to allow the fluids to cover a broader range of applications. Both monofunctional and difunctional derivatives have been produced. These fluids can be incorporated into various polymer systems including polyurethanes, epoxies, polyesters, polyacrylates, polyamides, and polyimides to modify the polymers and to give performance typically associated with fluoropolymers such as surface protection and abrasion resistance. Monofunctional fluids include silanes, phosphates, hydroxyl, carboxylic acid, alcohol, and amines. Difunctional derivatives include dihydroxyl, ethoxy ether, isocyanate, aromatic isocyanate, ester, and alcohols. The functionalities allow the various compounds to participate in a number of chemical reactions and to be used as surfactants and surface modifiers. The performance is obtained by having reactive end groups that can interact with other chemicals and additives in a way that is impossible for the inert PFPE molecule. In addition, emulsions in water have been made that are mixtures of water, ammonia, and PFPE derivatives.

III. PROPERTIES

PFPE oils are colorless and odorless fluids. Physical properties that vary with molecular weight are density, pour point, viscosity, viscosity index, volatility, and vapor pressure. Chemical properties and stability usually depend more on chemical structure than on molecular weight, so they do not vary with changes in molecular weight or viscosity.

A. Chemical Properties

1. Thermal and Oxidative Stability

The temperature at which thermal decomposition of the PFPE-K oils begins has been measured in our laboratory by differential thermal analysis. This method gives a value in excess of 470°C. PFPE impurities not removed by the manufacturer during purification can appreciably lower the temperature at which initial decomposition is observed. These impurities may be products of side or incomplete reactions during the manufacturing process. For this reason, a more useful value is obtained by determining the rate of degradation over a long period of time at a high temperature. Such an experiment was carried out by heating a sample of PFPE-K oil in an Inconel tube under an atmosphere of argon at 452°C for 31 days. The loss of oil averaged 1.1 wt % per day and the loss in viscosity was 3%. The oil as recovered was colorless and suffered little change in molecular weight. Table 1 summarizes available data on the temperature stability of PFPE by type.

PFPE oils are more stable in pure oxygen than they are in inert systems (Table 1). However, Sianesi et al. [10] showed that the decomposition temperature for PFPE-Y oils in air was very close to the thermal decomposition temperature in an inert atmosphere.

Results of tests with PFPE-K under a variety of conditions demonstrate the inertness of the PFPE oil to reaction with oxygen (Table 2). Shock loading tests of PFPE-K with gaseous oxygen ranging from 93°C and 7500 psi to 277°C and 6000 psi showed no reaction.

The thermal-oxidative stability of the PFPE polymer depends on its structure. The relative stability of each type of PFPE appears to be related to the degree of shielding of the ether linkage by pendant trifluoromethyl groups and to the presence of the difluoroformyl group on the polymer chain. Jones et al. [11] studied the effect of branching on the thermal oxidative stability of low molecular weight PFPE in the gas phase in glass ampules. Oxidative stability measurements seemed to indicate that highly branched PFPE oils are much less stable than PFPE molecules containing a repeating, single trifluoromethyl pendant group.

Impurities in the product can play an important role in the initial, apparent thermal-oxidative stability of the PFPE. Paciorek et al. [12] found that PFPE-K, PFPE-Y, or PFPE-Z (PFPE-D was not tested) oils that contained impurities initially appeared to be have poor thermal-oxidative stability. However, once the impurities had been removed or reacted away, the oil appeared to be significantly more stable until the upper temperature limit was reached. If these impurities are not removed during manufacturing, the apparent upper temperature limit of thermal-oxida-

Table 1 Stability of PFPE in Inert Atmosphere and Air

Type	Stability limit (°C)	
	Inert ^a	Air
PFPE-K	>450	400
PFPE-Y	<350	<300
PFPE-Z	NA	<288
PFPE-D	NA	370

Source: Individual manufacturers' reference literature

^a NA, data not available.

Table 2 Oxygen Compatibility Tests with PFPE-K

Test type	Temperature [°C (°F)]	Oxygen pressure [MPa (psi)]	Impact energy [J (ft-lb)]	Test result
Ignition in gaseous oxygen ^a	400 (752)	13 (1,886)		No ignition
Pressure drop in gaseous oxygen bomb ^b	99 (210)	0.7 (100)		No pressure drop after 600 h
Mechanical impact in liquid oxygen ^{c,e}	Ambient		98 (72)	No reaction in 20 trials
Mechanical impact in liquid oxygen ^a	Ambient		122 (90)	No reaction in 10 trials
Mechanical impact in liquid oxygen ^f	Ambient		736 (543)	No reaction in multiple trials

^aBritish Specification 3100.^bAmerican Society for Testing and Materials, D-942.^cMarshall Space Flight Center Specification 106B.^dNational Aeronautics and Space Administration Handbook, 8060.1B, Test 13, Part 1.^eAmerican Society for Testing and Materials, D-2512.^fWest German Federal Institute for Materials Testing (BAM), 8104-411.

tive stability can be much lower than that expected. The decomposition products do not appear to promote or catalyze further degradation of the PFPE when the reaction is performed in glass.

Gumprecht [13,14] reported that $\text{CF}_3\text{CF}=\text{CF}_2$, CF_3COF , and COF_2 were the main products in the thermal decomposition of PFPE-K. Paciorek et al. [15] found SiF_4 , CO_2 , and some BF_3 when oxygen was present. In the presence of oxygen, SiF_4 and BF_3 are formed by reaction with the glass ampule walls.

Other studies confirm the effect of structure on the thermal oxidative stability of PFPE oils. Paciorek et al. [15] found PFPE-K to be stable in the presence of oxygen to the highest temperature tested ($>340^\circ\text{C}$). However, Jones et al. [16] found that PFPE-Z is inherently unstable at 316°C in oxidizing atmospheres. Neither hydrogen-end-capped polymer nor polymer with remaining peroxide linkages is the cause of this apparent instability. The instability has been attributed to the presence of the difluoroformyl ($-\text{CF}_2\text{O}-$) and tetrafluoroethylene oxide ($-\text{CF}_2\text{CF}_2\text{O}-$) units in the polymer chain. These same difluoroformyl groups are also present in PFPE-Y. In fact, Pearson et al. [17] report that in the temperature range $325-405^\circ\text{C}$ in a Monel vessel, PFPE-Y, which contains the difluoroformyl group, decomposes 20–40 times faster than PFPE-K. These observations are consistent with the theory that the difluoroformyl groups contribute to instability of the PFPE at higher temperatures.

PFPE oils leave no deposits when they volatilize. Even when PFPE molecules thermally decompose, tars or residues are not observed. Generally the volatile decomposition products are removed as they are formed. If such decomposition products are not removed, PFPE decomposition products may react with the surface in contact with the PFPE. In contrast, hydrocarbon lubricants thermally form gums or oxidatively decompose or polymerize to form tars, or deposits. These hydrocarbon-derived deposits then cause problems that can lead to apparent lubricant failure. The oxidation stability of PFPE oils is perhaps best demonstrated on a practical basis by the practice of purifying samples of the oil contaminated with traces of hydrocarbon oils by blowing air through the mixture at high temperatures (300°C and up) for several hours. Under

these conditions, the hydrocarbons are oxidized and the PFPE oils can be recovered in a pure state by filtration.

2. Lewis Acid Stability

Metal fluorides can catalyze the decomposition of PFPE oils, especially those PFPE oils that contain the difluoroformyl ($-\text{CF}_2\text{O}-$) group. PFPE lubricants will react with Lewis acids, such as aluminum trichloride, at temperatures normally considered safe for PFPE oils [18]. The apparent catalytic activity of the Lewis acid depends on the PFPE structure type. Polymers that contain the difluoroformyl group appear less stable than those without it [12]. PFPE-Z is stable up to 260°C in contact with metals but is not stable at temperatures even less than 100°C in the presence of metal halide Lewis acids [19].

Metal halides, such as AlCl_3 , catalyze the decomposition of PFPE oils of all types. PFPE-Y and PFPE-Z, which contain the difluoroformyl group, decompose more rapidly than PFPE-K or PFPE-D, which do not contain that group. The effect of aluminum trichloride on the stability of different PFPE is shown in Fig. 1.

Sianesi et al. [10] showed that metal oxides can also lower the decomposition temperature of PFPE-Y. Cuprous oxide had a small effect on the rate of decomposition at 360°C , whereas aluminum oxide had 100 times that rate. The data are summarized in Table 3.

Carre and Markowitz [20] demonstrated that iron fluoride can form in the raceways of bearings lubricated with PFPE and that the presence of FeF_3 can lower the temperature at which the polymer begins to decompose. Unfortunately, the PFPE type is not disclosed, and the magnitude of this effect is difficult to evaluate.

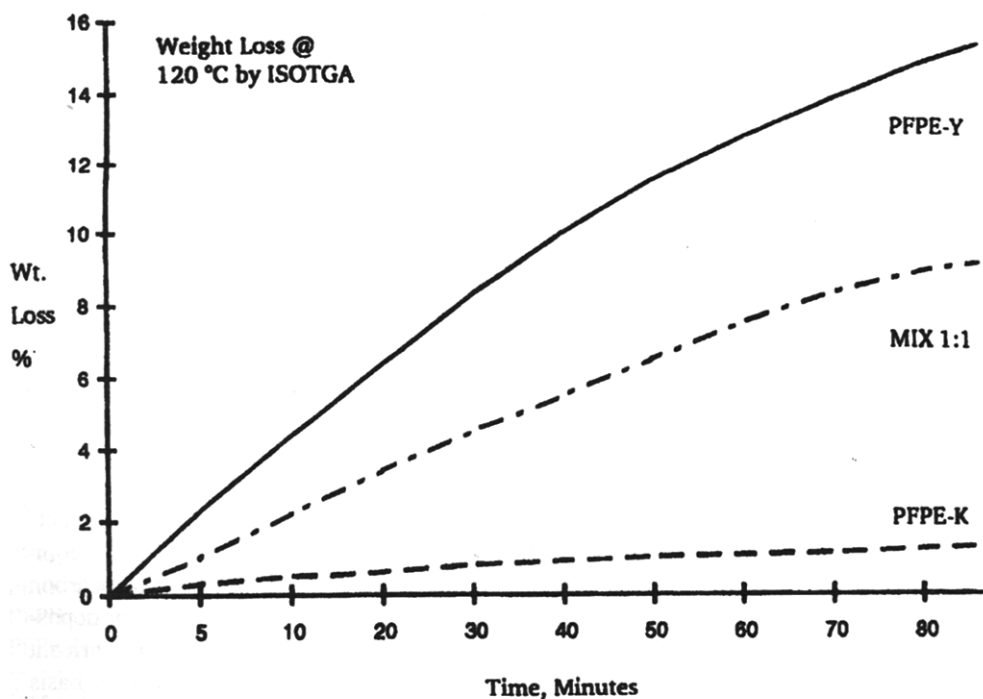


Figure 1 Effect of Lewis acids on PFPE degradation.

Table 3 Weight Loss of PFPE-Y per Minute, Exposure at 360°C

Metal oxide	Rate (% wt loss/min)
ZrO ₂ , CrO ₃ , SnO ₂ , WO ₃ , ThO ₂ , Al ₂ O ₃	>5
CeO ₂ , TiO ₂	1–5
Fe ₂ O ₃ , NiO	0.5–1.0
V ₂ O ₅ , MgO	0.3–0.5
Cr ₂ O ₃ , Sb ₂ O ₃ , Co ₃ O ₄ , Ga ₂ O ₃ , 12% H ₂ O	0.15–0.3
CuO, MoO ₃ , HgO, ZnO, SnO, MnO ₂ , TeO ₂ , BaO, CaO, SiO ₂ , In ₂ O ₃ , GeO ₂ , Bi ₂ O ₃ , P ₂ O ₅ , PbO	0.09–0.15
Cu ₂ O	0.05
Inert gas, N ₂	<0.02

3. Compatibility of PFPE Fluids with Metals and Metal Compounds

A summary of metals compatible with PFPE oils at various temperatures is given in Table 4. In the presence of oxygen, oxidative corrosion may occur with some metals. PFPE-K oils are inert to most metals at temperatures up to approximately 288°C in an oxygen atmosphere. Compatibility results of PFPE-K oils with a number of metals and alloys, using the “microoxidation–corrosion test” developed by the Air Force Materials Laboratory are shown in Fig. 2. In general, nickel and cobalt alloys exhibit the greatest resistance to oxidative corrosion and are suitable

Table 4 Metals and Alloys Suitable for Use with PFPE-K Oils at Elevated Temperatures^a

Temperature	Air atmosphere
371°C (700°F)	Nickel alloys Cobalt alloys AMS-5547 steel
343°C (650°F)	AMS-5525 steel Titanium alloy Ti(6Al 6V 2Sn); Mg, Ag, Cr, V
316°C (600°F)	301, 304, 310, 316, 321, 446 N-155 Titanium alloy Ti (13V – 11Cr 3Al) Titanium alloy Ti (6Al 4V) Aluminum alloy Al (QQ-A-355) Bearing bronze
288°C (550°F)	405, 410, 440 stainless steels QQS-636, M-1, M-50, WB-49, 52100 steels Ti (8Mn) Copper
288°C	Most metals and alloys show little or no evidence of corrosion.

^aTest conditions: 72 hours at 5 L dry gas/h; qualifying corrosion rate, <0.4 mg/cm/day.

Note: Any metal or alloy suitable at one temperature is also suitable at all lower temperatures.

Any metal suitable in air is also suitable in inert atmosphere.

Source: DuPont literature.

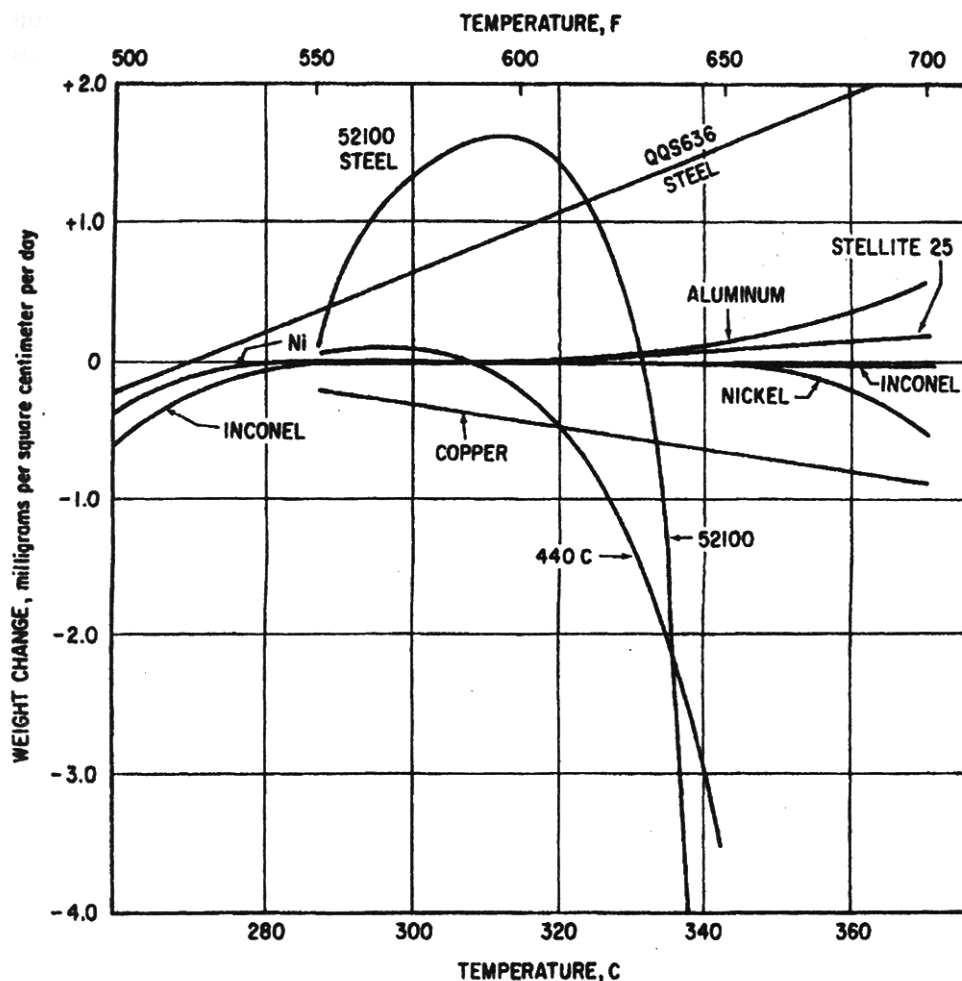


Figure 2 Corrosion of metals by PFPE-K at elevated temperatures.

for use with PFPE oils up to at least 370°C. Ordinary steels are not suitable above 288°C. Specific stainless steels are satisfactory at 316°C.

Certain alloys cause catalytic depolymerization of PFPE oils at high temperatures. Titanium alloys that contain aluminum can decompose PFPE oils above 136°C. Aluminum 2024 appears to do the same thing at 370°C. These problems are greatly minimized in the absence of oxygen, indicating that the reactions involved are between the oil and oxide coating on the metals.

Additives that markedly decrease the reaction rate of PFPE oils with many metals at high temperatures are under development [9,21]. Some offset the catalytic depolymerization of the oils caused by titanium alloys [16,22–26].

4. Hydrolytic and Chemical Stability

Hydrolytic stability of PFPE oils is exceptional. Long-term contact with steam or boiling water produces no adverse effects on the PFPE fluids.

All PFPE oils are essentially inert to most chemicals. No reaction is observed with boiling sulfuric acid, fluorine gas at 200°C, molten sodium hydroxide, chlorine trifluoride at 10–50°C,

uranium hexafluoride gas at 50°C, or any of the following materials at room temperature: JP-4 turbine fuel, unsymmetrical dimethyl hydrazine, hydrazine, diethylenetriamine, ethyl alcohol, aniline, 90% hydrogen peroxide, inhibited red fuming nitric acid, and nitrogen tetroxide. PFPE-K oils are slightly soluble in hydrazine and have moderate (25–30%) solubility in nitrogen tetroxide.

Again, there may be stability differences depending on the type and structure of the PFPE. PFPE-Y is reported to react with liquid (100%) and gaseous ammonia, alkaline metals, and finely divided powder of light metals such as aluminum, magnesium, and their alloys [27]. Table 5 summarizes PFPE-Y reactivity data. In comparison to the reactivity of PFPE-Y, PFPE-K has shown no reactivity toward ammonia (personal observation). Although there are no available data on the reactivity of PFPE-K with alkaline metals, all PFPE molecules will probably react with nascent metal surfaces and unpassivated metals that are high in surface area.

5. Solubility

PFPE oils are not soluble in common solvents, acids and bases, but some solvents will dissolve in PFPE oils. Table 6 shows solubility data for PFPE-Y. PFPE oils are completely miscible in highly fluorinated solvents such as trichlorotrifluoroethane, hexafluorobenzene, perfluorooctane, perfluorohexane, hexafluoropropylene dimer, 2,3-dihydrodecafluoropentane, perfluorodimethylcyclobutane isomers, and 1,1 dichloro-1-fluoroethane. PFPEs are also soluble in supercritical CO₂. Table 7 summarizes gas solubility data.

6. Compatibility with Elastomers and Plastics

Elastomer compatibility with PFPE-K oil is summarized in Table 8 [28]. Most elastomers are affected only slightly by contact with the oil at 93°C. The inherent stability of the elastomers themselves, rather than incompatibility with PFPE, limits their use at higher temperatures. No significant changes in dimension, hardness, or color were noted when selected elastomers were immersed in PFPE oil at 70°C for 6 months [29]. Elastomers used in this test were neoprene, butyl, Buna-N, natural rubber, polyfluorosiloxane, polychlorotrifluoroethylene, and vinylidene fluoride–hexafluoropropylene copolymers.

PFPE oils have no significant effect on plastics. The following showed no effect when treated with PFPE-Y for 1000 hours at 70°C: acetal copolymer (POM), acrylonitrile–butadiene–styrene copolymer (ABS), phenylene-oxide based resins (PPO), polyamide 66 (Nylon 66), poly-butylene terephthalate (PBT), polycarbonate (PC), high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA),

Table 5 Chemical Resistance of PFPE-Y Oils

Chemical type	Chemical name	Temperature (°C)
Organic solvents	All common	300
Organic acid	Carboxylic acids	300
Organic base	Tributylamine	200
Inorganic acid	HF, H ₂ SO ₄ , HCl	300
Inorganic base	KOH, NaOH,	200
Inorganic salt	NaCl, KF	250
Oxidizing agent	Br ₂ , Cl ₂ , F ₂	250
Oxidizing agent	KMnO ₄ , K ₂ CrO ₄	200
Lewis acid	AlCl ₃	200
Lewis acid	FeCl ₃	200

Source: Montedison literature.

Table 6 Solubility^a of Common Solvents and PFPE-Y Oils

Solvent	Solubility of PFPE in solvent	Solubility of solvent in PFPE	Amount of solvent in 100 g PFPE (g)
Hexane	SS	PS	2.0
<i>n</i> -Heptane	PS	SS	1.6
<i>n</i> -Octane	I	I	—
Cyclohexane	I	I	—
Benzene	I	SS	1.3
Toluene	I	I	—
Xylene	I	I	—
Ethyl ether	SS	PS	2.6
Tetrahydrofuran	I	SS	1.4
Ethyl acetate	I	I	1.5
Methyl formate	I	I	—
Dimethyl ketone	I	I	—
Methylethyl ketone	I	I	—
Trichloroethylene	I	PS	3.0
Monochlorobenzene	I	I	—
Chloroform	SS	PS	4.1
Carbon tetrachloride	SS	PS	2.9
Perfluoroalkanes	Miscible	Miscible	—

^a SS, slightly soluble, PS, partially soluble; I, practically insoluble.

Source: Montedison literature.

polypropylene (PP), polystyrene (PS), high impact polystyrene (HIPS), polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), polyvinylidene sulfide (PVDS), and styrene-acrylonitrile copolymer (SAN).

7. Flammability

PFPE-K oils are not flammable under any conditions likely to be encountered. They show no autogenous ignition, flash, or fire points up to 649°C (1200°F) in standard ASTM tests. A sample

Table 7 Gas Solubility in PFPE-Y at 20°C

Type of gas	Gas/mL PFPE-Y (mL)	Gas (ppm)
Helium	0.08	8
Hydrogen	0.09	4
Oxygen	0.290	218
Nitrogen	0.190	125
Carbon dioxide	1.30	1344
Chlorine	3.189	5320
Fluorine	0.197	176
Hydrogen fluoride	0.806	379
Water vapor	0.04 ^a	17

^a Estimated from water solubility.

Source: Montedison literature.

Table 8 Elastomer Compatibility^a with PFPE-K Oil Based on 168 hours of Tests at Three Temperatures

Elastomer	At 93°C	At 149°C	At 204°C
Fluorosilicone	S	S	NG
Ethyl acrylate	S	S	NG
Methyl silicone	S	S	NG
Viton®, fluoroelastomer	S	S	S
Urethane	S	—	—
Hypalon®, synthetic rubber	S	NG	—
Butyl 325	S	NG	—
VPA	S	NG	—
Natural rubber	NG	—	—
Neoprene®, WRT	S	NG	—
Hycar 100 (Buna N)	S	—	—
Polysulfide (Thiokol)	S	—	NG
cis-1, 4-Polybutadiene	NG	—	—
Synpol 1013, SBR	NG	—	—
EPT, sulfur cure	S	—	NG
EPT, peroxide cure	S	S	NG
Polypropyleneoxide, XP-139	—	NG	—
Cyanacryl, acrylic rubber	—	S	NG
Teflon®	S	—	S

^aS, only minor changes in elastomer properties; NG, major, generally harmful, effect on elastomer properties.

Source: Personal data and DuPont literature.

of PFPE-K did not flash or burn when contacting a manifold at temperatures in excess of 649°C (1200°F). In a high pressure spray ignition test (MIL-F-7100), PFPE-K oil did not flash or fire at up to 2 feet from the spray orifice.

8. Radiation Resistance

Compared with many materials used as lubricants or power fluids, PFPE-K oils are stable to radiation. In general, irradiation of PFPE-K oils causes only minor changes in its physical properties. No insoluble solids or sludge are formed, and the viscosity decreased 21% when a sample of PFPE-K was exposed to 10⁸ rads of electron bombardment at ambient temperature in air.

Mori and Morales [26] studied the effects of x-ray irradiation on the degradation of PFPE-D, PFPE-Z, and PFPE-K. They concluded that PFPE-D cross-links more easily than the other fluids.

9. Shear Stability

PFPE-K oil did not break down when subjected to high rates of shear. Exposure at 10 kHz in a sonic shear tester (ASTM D-2603) at room temperature for one hour resulted in viscosity changes of less than 0.5%. The sonic test is severe and is very effective in breaking down polymers typically used as viscosity index improvers in lubricating oils of various types.

B. Physical Properties

The physical properties of PFPE oils that show little change with molecular structure are summarized in [Table 9](#).

Table 9 Typical Properties of PFPE Oils

Property	PFPE-K	PFPE-Y	PFPE-Z	PFPE-D
Density, g/mL	1.86–1.91 at 24°C	1.86–1.91 at 20°C	1.82–1.85 at 20°C	1.86–1.89 at 20°C
Refractive index	1.29–1.301 n_D^{24}	1.29–1.304 n_D^{20}	1.29–1.294 n_D^{20}	1.29–1.298 n_D^{20}
Surface tension, mN/m	16–20	18–21	23–24	17.7–19.1
Isothermal secant	1034 Mpa at 38°C	9650 kg/cm ² at 25°C	ND	ND
Bulk modulus	34.5 MPa	100 kg/cm ²	ND	ND
Coefficient of thermal expansion, °C ⁻¹	0.00095–0.00109	0.00092–0.00109	ND	ND
Specific heat, cal/g/°C, 38°C	0.23–0.24	0.24	0.20–0.23	ND
Thermal conductivity, W/(m · K) at 38°C, 0.0692–0.0883 W/(m · K) at 260°C	0.0831–0.0934	ND	ND	ND

Source: Product literature (DuPont, Daikin, Montedison).

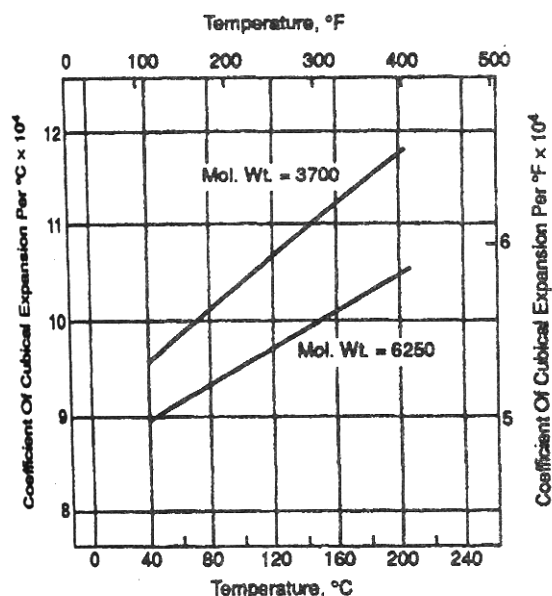


Figure 3 Thermal coefficient of expansion for PFPE-K oils.

1. Thermal Properties

Thermal conductivity of PFPE-K varies slightly over a wide temperature range. These values are a little lower than many hydrocarbon lubricants with similar viscosity. The specific heat of PFPE-K with number-average molecular weight of 6000 amu is a linear function of temperature varying from 0.23 to 0.24 cal/g/°C at 38°C to 0.29 to 0.30 cal/g/°C at 204°C. Thermal coefficients of expansion for two PFPE-K oils are given in Fig. 3. The thermal coefficient of expansion and its change with temperature decrease with increasing molecular weight.

2. Density

The densities of PFPE fluids are nearly twice those of hydrocarbon lubricants. Density increases slightly with increasing molecular weight and decreases linearly with temperature.

3. Electrical Properties

Electrical properties (Table 10) are affected by the presence of even trace amounts of moisture in the PFPE oil. The values will be lower for lower molecular weight/viscosity materials and will increase as molecular weight increases.

Table 10 Electrical Properties of PFPE Oils at 25°C

Property	PFPE-K	PFPE-Y	PFPE-Z
Dielectric breakdown voltage, ASTM D-877, kV/0.1 in.	38.8–41.1	40	30
Specific resistivity, ASTM D-257, $\Omega \cdot \text{cm}$	6×10^{13} – 4×10^{14}	10^{15}	4×10^{13}
Dielectric constant, ASTM D-150 at 10^2 – 10^5 Hz	2.10–2.15	2.1–2.3	2.0
Dissipation factor, ASTM D-150 at 10^2 – 10^5 Hz	<0.003 – <0.007	4×10^{-4}	5×10^{-4}

Source: Manufacturers' literature.

4. Vapor Pressure and Volatility

The vapor pressure and volatility of PFPE oils at a specific temperature vary inversely with average molecular weights. Thus the higher viscosity oils generally have lower volatility losses.

The vapor pressure of a PFPE fluid can be very sensitive to the presence of small amounts of impurities, such as very low molecular weight fractions or solvents. The Isoteniscope method is very sensitive to the presence of small amounts of high vapor pressure impurities, whereas the Knudsen method is not. Comparing the vapor pressure obtained by both methods indicates the level of these impurities. The Knudsen method is normally reported in the literature and in manufacturers' information bulletins.

The vapor pressure and viscosity of specific homologues of PFPE will be dependent on molecular weight. Commercial PFPE products may appear to contradict this correlation because different grades with the same viscosity have different vapor pressures. Commercial PFPE oils are composed of distributions of different molecular weight polymers, and the fraction of lower molecular weight polymer will determine the vapor pressure of that grade. Oils made specifically for vacuum systems are carefully distilled to remove low molecular weight fractions, which gives them superior vapor pressure.

Volatility, as measured by ASTM D-972, is shown in Table 11. In this test, a steady stream of air is blown across the surface of the hot oil, and the results are useful in determining the light-end content of the particular oil. As the lower molecular weight polymers evaporate, the viscosity of the oil increases.

5. Viscosity

The viscosity of PFPE oils and their change with temperature for each type of PFPE are shown in Fig. 4. The absolute or centipoise millipascal-second viscosity will be 1.9 times higher than the kinematic viscosity because the density of PFPE oils is about 1.9 g/mL. The temperature dependence of viscosity (i.e., viscosity index) is similar to that of high grade petroleum oils with the exception of PFPE-Z, which has a VI more favorable than that of petroleum oils.

PFPE oil viscosity increases with an increase in the molecular weight. Commercial PFPE polymers are fractionated by distillation to produce a series of grades, based on viscosity. The viscosity is a function of average molecular weight, and the same viscosity can be obtained from a very narrow or a very broad molecular weight distribution.

Cantow and Barrall and their associates [30] examined the dependence of the viscosities of PFPE fluids on temperature and pressure and found that differences could be attributed to

Table 11 Evaporation of PFPE-K Oils (ASTM-D972)

MW	Loss (wt %)						
	In 6.5 h test				In 22 h test		
	99°C	149°C	204°C	260°C	149°C	204°C	260°C
1850	<1	10	60	—	20	80	—
2450	<1	5	30	—	5	40	—
3000	<1	1	10	45	3	20	60
3700	<0.1	1	5	30	1	5	40
4800	<0.1	<1	1	15	—	2	20
6250	<0.1	<1	1	4	—	1	6
8250	<0.1	<1	<1	2	—	—	3

Source: DuPont data

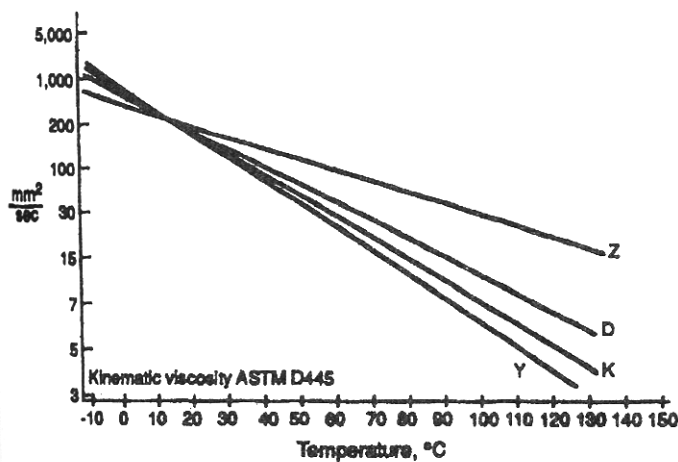


Figure 4 Viscosity-temperature properties: comparison of different PFPE types.

structural differences. The bulky CF_3 groups are responsible for the high pressure sensitivity of the nonlinear PFPE and the lower viscosity index.

6. Compressibility

PFPE oils are considerably more compressible, with lower bulk modulus, than conventional petroleum hydraulic fluids. Adiabatic tangent bulk modulus data (obtained by sonic methods) for PFPE-K are given in Fig. 5 for pressures up to 34.5 MPa (5000 psi) and temperatures to

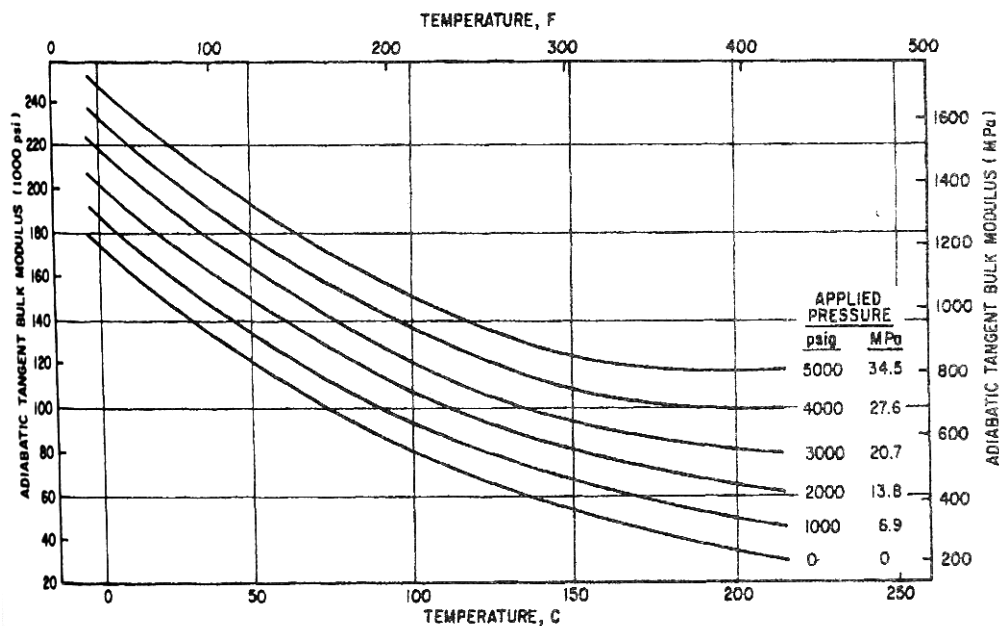


Figure 5 Adiabatic tangent bulk modulus of PFPE-K fluorinated oil.

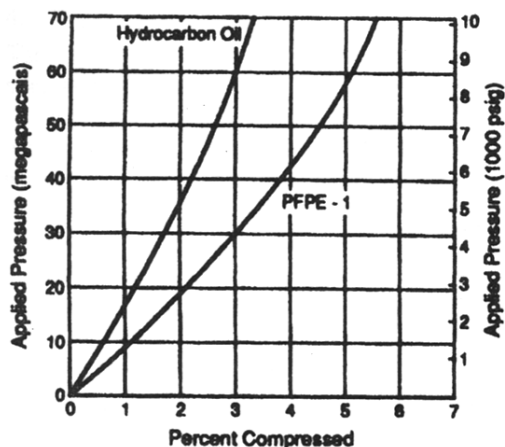


Figure 6 Compressibility of hydrocarbon oil and PFPE-K at 38°C.

204°C (400°F). Figure 6 compares the compressibility of PFPE-K fluorinated oil with that of a typical hydrocarbon-based hydraulic fluid. At 38°C (100°F) and an applied pressure of 34.5 MPa (5000 psig), the hydrocarbon oil volume is reduced by about 2%, while PFPE-K is compressed almost 3.5%.

C. Lubrication Performance

PFPE oils are excellent lubricants under normal, severe, and starved operating conditions; they also perform well under heavy loads, at high speeds, and at elevated temperatures. In general, when failure does occur, it occurs over a period of time, giving the operator warning. Test data in the following lubricity tests were obtained on PFPE-K oil that contained no additives.

1. Four-Ball Wear and Extreme Pressure Tests

Four-ball wear tests were conducted on PFPE-K at 75 and 316°C and at loads of 1–40 kg using balls made of different alloys. Typical results at 620 and 1280 rpm are given in Fig. 7. Table 12 shows the load-carrying ability of PFPE oils in four-ball EP tests and how it increases with viscosity.

2. Falex Extreme Pressure Tests

Extreme pressure tests with the Falex pin and V-block tester (Table 13), using M-10 or 52100 steels with PFPE oils, exceeded the limits of the test equipment. When the standard shaft and V-block metals were used, the load at failure for PFPE oil far exceeded that of the non-PFPE test oils.

3. Bearing Fatigue Tests

Fatigue test results in a rolling contact bearing rig in Table 14 showed PFPE oil to have excellent fatigue life at room temperature and at 218° and 316°C. The test pieces were made from M-50 steel; the stress was 4826 MPa (700,000 psi) maximum hertz, and the speed was 25,000 stress cycles per minute. Oil was fed at the rate of 20 drops per minute.

4. Comparative Performance Data

The chemical resistance of the PFPE lubricants (oils and greases) has led to their widespread use in many applications in the space programs, where complete inertness to fuels and oxidants

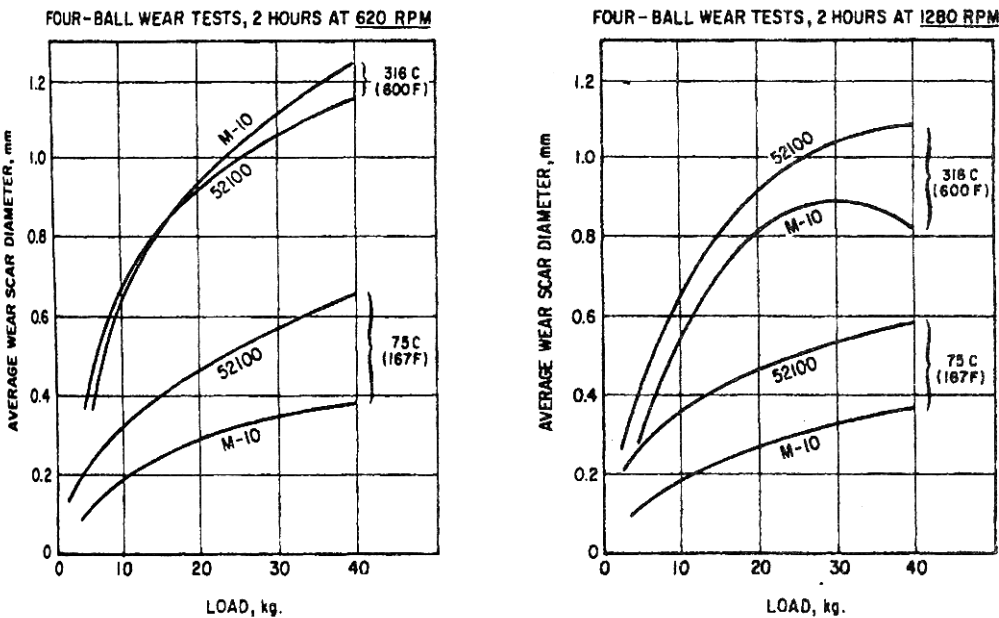


Figure 7 Wear characteristics of PFPE-K oil.

is vital. Thus, both the oils and greases have been used to lubricate O-rings in many applications on the Apollo and other space projects. In general, a lighter oil is used if the O-rings are expected to operate after assembly. If the O-ring is static and lubricant is required solely to assist in assembly, a grease made from one of the heavier oils is preferred because of its lower volatility. Both oils and greases have been used as lubricants and antiseize compounds in the assembly of threaded fittings on spacecraft.

PFPE oil is used on the fasteners and moving parts of astronauts' pressure suits, largely because of its nonflammability. The same oil has been used successfully on the bearings of antenna arrays on spacecraft. This oil has also proved satisfactory in lubricating bearings that permit extension of the paddle arms supporting solar cells on other spacecraft. PFPE is also

Table 12 Extreme Pressure Lubricating Characteristics of PFPE-K Oils, Four-Ball Test*

Oil	Viscosity at 38°C (cSt)	Mean Hertz load (kg)	Incipient seizure (kg)	Weld point (kg)
PFPE				
MW 1850	18.1	45.9	141	200
MW 3700	87.0	62.3	200	224
MW 6250	280.0	98.0	200	398
Di-2-ethylhexyl sebacate	12.3	15.1	40	89
Silicate ester fluid	33.0	20.9	63	100
Phosphate ester fluid	11.5	25.3	79	112
EP petroleum gear oil	35.3	64.4	89	398

*Four-ball load-carrying capacity test (mean Hertz load) by FTMS-791 method 6503.1.
Source: DuPont product literature.

Table 13 Extreme Pressure Characteristics of PFPE-K Oil, Falex Pin and V-Block Test^a

Oil	Specimen material		Maximum normal conditions		Failure load (kg)
	Shaft	V-Blocks	Load (kg) ^b	Torque (J)	
PFPE-K, MW 6250	SAE 3135	AISI 1137	1814	5.88	1928 ^c
PFPE-K, MW 6250	52100	52100	2041	5.42	No failure
PFPE-K, MW 6250	M-10	M-10	2041	4.29	No failure
Deep dewaxed Mineral oil	SAE 3135	AISI 1137	454	2.83	567 ^d

^a Using the Falex Pin and V-Block Tester; test conditions, load increased by 250 lb increments every minute.

^b 2041 kg capacity gauge.

^c Load dropped.

^d Shaft fractured.

Source: DuPont product literature.

used as the lubricant for the slide wire of potentiometers installed in spacecraft. The oil minimizes wear and does not migrate to other parts of the system.

In nuclear power plants, PFPE was used as a bearing lubricant for pumps operating in an area in which it was exposed to radiation. In this case, the radiation rapidly decomposed ordinary petroleum oils, but the PFPE oil operated for long periods of time without appreciable decomposition. In one instance, after 900 hours of operation the viscosity had changed only 2%, and no sludge or gum had formed.

The PFPE oils, because of their excellent stability to oxidation and the absence of gum formation, are used as lubricants for the bearings, jewels, and pivots of instruments of many different kinds. The shelf life for PFPE oils is nearly indefinite.

In an office machine, a lightly loaded size R-6 bearing was placed near an electrical heating element and often reached temperatures greater than 260°C. This bearing, operating at 500 rpm, failed in less than 500 hours with all MIL-G-25013 (dye-thickened, silicone-based) greases that were tested. This operating life was considered inadequate for the purpose. When PFPE grease was used as the lubricant, operating times in excess of 5000 hours were obtained.

Premature failure of the bearings of a synchronous electrical motor in a plant that produces

Table 14 Roller Contact Fatigue Tests^a

Temperature [°C (°F)]	Bearing life	Cycles ^b	
		PFPE-K	MIL-L7808 oil
32 (90)	B10	3.3×10^6	2.65×10^6
32 (90)	B50	10.1×10^6	6.5×10^6
218 (425)	B10	7.2×10^6	2.8×10^6
218 (425)	B50	13.5×10^6	7.0×10^6
316 (600)	B10	8.4×10^6	—
316 (600)	B50	18.1×10^6	—

^a Test specimens, M-50 steel bars and rollers; 65,000 psi (448 MPa) maximum Hertz load.

^b Minimum 25,000 stress cycles, maximum 700,000 psi (4,826 MPa) Hertz stress, air.

Source: DuPont data.

synthetic textile fibers occurred when a dye-thickened, silicone-based grease was used. The size 210 shielded cartridge-width ball bearings operating at 3200 rpm at about 375°F failed in 2–6 months, for an average life of 2.5 months. When PFPE grease was substituted for the silicone grease, bearing life increased to an average exceeding 1 year.

In a machine designed to orient polypropylene film at a temperature of 150°C, the film is held in position by stud-mounted, sealed roller bearings of 0.5 in. bore. When these bearings were lubricated with a high quality diester-type grease, the incidence of bearing failure reached an intolerable level, and production downtime became excessive. Introduction of a dye-thickened silicone grease improved but did not solve the problem. PFPE grease was then adopted with appreciable improvement in performance, and it has been in use at this plant for many years.

The sealed rolling element bearings on a track and chain conveyor in another plant, one that manufactures polyester film, operate in an oven at 260°C. The use of a silicone grease thickened with carbon black led to many premature bearing failures because the grease tended to run out of the bearings past the seal. This problem was solved by the use of PFPE grease, which has performed satisfactorily at this plant for many years.

A battery of 7.5 hp electrical motors is used to drive centrifugal-type blowers circulating hot air in a chemical drying process unit. The ambient air temperature in the vicinity of the motor bearings is about 250°C. The bearing nearest the blower is a size 310 shielded ball bearing, and the one on the opposite side is a 35 mm (6207 size) bore roller bearing. When these bearings were lubricated with a premium quality, high temperature bearing grease, bearing failures reduced motor life expectancy to less than 12 weeks. Bearing failure appeared to be due to lubrication starvation caused by the grease melting and running out of the bearing and by the formation of grease deterioration products within the bearing. When PFPE grease was adopted, average motor life increased to over 36 weeks, and any failure were due to mechanical parts, not the grease.

5. PFPE Greases

The PFPE oils can be used directly as lubricants, or they can be used as the base oils for making greases. The principal advantage of the greases over the oils is that greases will “stay put” on surfaces where the oils might tend to run off or drain away rapidly.

A large number of solids are suitable thickening agents for the formation of greases from the PFPE oils. Many of the thickening agents used for PFPE greases are the same as those used for hydrocarbon greases. Hydrocarbon soaps are not used because their thermal and chemical stability is poor. Thickening agents commonly used are finely divided silica, “Attapulugus clay,” montmorillonite, ammeline, boron nitride, copper phthalocyanine, metal-free phthalocyanine, the PTFE family of polymers, fluorinated ethylene–propylene copolymers, and zinc oxide.

Some thickeners or fillers have been described as imparting thermal conductivity to the grease. For instance, a grease made with PFPE-Y and boron nitride has a coefficient of thermal conductivity of 0.68 and also possess good heat and acid resistance [31]. Some of the PFPE greases thickened with fluorinated ethylene–propylene copolymer or PTFE contain antioxidants [32] such as tris(fluoroalkoxyphenyl)phosphine or corrosion inhibitors such as benzimidazole derivatives [33], perfluoroalkyl- and perfluoroalkyl-ether-substituted benzoxazoles, benzothiazoles, bisbenzoxazoles, and bisbenzothiazoles [24]. Some PFPE greases are prepared by polymerizing tetrafluoroethylene in the perfluoroalkylpolyether [34].

Ball bearing performance tests on the PTFE-thickened PFPE-K greases using FTMS-791, method 333, show that PTFE-thickened PFPE greases give excellent high temperature performance. Results in Table 15 are reported in hours to failure (as evidenced by excessive running torque with a large increase in spindle input power, excessive bearing noise or screech, or increase of more than 20°F in bearing temperature).

Table 15 Performance of PFPE-K Grease in Ball Bearings

PFPE Grease	Temperature (°C)	Speed (rpm)	Hours to failure
A	204	20,000	>500
B	204	20,000	>500
A	260	10,000	>500
B	260	10,000	>2000
B	288	10,000	>500

Source: DuPont product literature.

IV. MANUFACTURERS, MARKETING, AND ECONOMICS

A. Oil Producers

Four companies make all the PFPE oils in the world: Du Pont in the United States, Montedison in Italy, Daikin in Japan, and NOK in Japan. The total production of PFPE oils is very difficult to determine, but surely exceeds 1000 tons/year.

Information about the fraction produced by each company is not readily available. Within the last 10 years, Daikin reported a 60 metric tons per year fluorine oil plant, and Asahi Glass reported a 50 tons per year fluorinated oil plant.

The Appendix lists standard commercially available fluids. The soluble and functional fluids are too complex to list here, but information about their properties is available from the manufacturers.

B. Marketing

The manufacturers sell the oils directly and also produce their own brands of grease. Much of the oil goes directly into vacuum pump fluid use. In addition, the oils are often sold to specialty lubricant suppliers around the world who formulate the oils into greases which they sell under their own brand names. Because soluble oil additives are relatively recent developments, formulated oils have not been supplied in the past.

C. Economics

The notion that these lubricants are prohibitively expensive or can be used only in very special situations is false. The lowest selling price is under \$100/lb and the highest is over \$3000/lb. PFPE oils and greases can be used for general-purpose lubrication, especially in the presence of severely harsh and demanding environments. These products are often the most cost-effective solution, even though the initial price is higher. They can significantly reduce costs by increasing the relubrication time interval and reducing the labor costs. The longer life and higher load-carrying capability gives longer equipment life, which reduces overall cost. The additional safety derived from a completely nonflammable lubricant that works at extremely high temperatures also increases the value of the product.

Because the oils can be regenerated by the manufacturers to new condition at a relatively low cost, the lifetime cost of the oils can be significantly reduced. The regenerated oils perform the same as new after regeneration, and regeneration eliminates the need to dispose of used oils.

V. OUTLOOK

The use of these fluids is increasing. As designers reduce the size of components in automobiles, trucks, heavy equipment, computers, and other common devices, the internal temperatures increase and conventional lubricants that have been used for years begin to fail. Often, the only fluids with the capability to handle the temperatures are PFPEs. In many cases in the automotive/transportation business, manufacturers have increased warranties and now require lubricants with longer life. Additionally, new jet engines are being developed that run at temperatures above the capabilities of currently used turbine oils but are within the range of PFPE oils. These new turbines promise significantly enhanced fuel economy and performance.

As new technology evolves, demands on conventional lubricants will continue to become more severe. This creates a continuing demand for the high temperature capabilities, nonreactivity, and long life of PFPE lubricants.

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Appendix 1 Commercially Available Fluids and Properties

Lubricating oils						
PFPE type	Average molecular weight	Viscosity (cSt)			Viscosity index	Pour point (°C)
		At 20°C	At 40°C	At 100°C		
PFPE-K-100	1,350	7	4	—	—	< -70
PFPE-K-101	1,500	16	8	2	—	< -70
PFPE-K-102	1,750	36	15	3	59	-63
PFPE-K-103	2,300	80	30	5	121	-60
PFPE-K-104	3,100	180	60	9	124	-51
PFPE-K-105	5,000	550	160	18	134	-36
PFPE-K-106	6,250	810	240	25	134	-36
PFPE-K-107	8,250	1600	440	42	155	-30
PFPE-Y-04	1,500	38	15	3.2	60	-58
PFPE-Y-06	1,800	60	22	3.9	70	-50
PFPE-Y-25	3,200	250	80	10	108	-35
PFPE-Y-45	4,100	470	147	16	117	-30
PFPE-YR	6,250	1200	345	33	135	-25
PFPE-YPL-1500	6,600	1500	420	40	135	-25
PFPE-YR-1800	7,250	1850	510	47	135	-20
PFPE-Z-03	4,000	30	18	5.6	317	-90
PFPE-Z-15	8,000	160	92	28	334	-80
PFPE-Z-25	9,500	260	159	49	358	-75
PFPE-Z-60	13,000	600	355	98	360	-63
PFPE-D S-20	2,700	53	25	—	150	-75
PFPE-D S-65	4,500	150	65	—	180	-65
PFPE-D S-100	5,600	250	100	—	200	-60
PFPE-D S-200	8,400	500	200	—	210	-53

Vacuum pump fluids				
PFPE type	Average molecular weight	Viscosity at 20°C (cSt)	Vapor pressure (torr)	
			At 20°C	At 100°C
PFPE-K-1506	2,400	62	4×10^{-7}	1×10^{-3}
PFPE-K-1514	3,500	142	2×10^{-7}	1×10^{-4}
PFPE-K-1525	4,600	261	1×10^{-7}	3×10^{-5}
PFPE-K-16256	11,000	2717	3×10^{-14}	1×10^{-9}
PFPE-Y-06/6	1,800	60	2×10^{-6}	5×10^{-3}
PFPE-Y-14/6	2,500	140	2×10^{-6}	2×10^{-3}
PFPE-Y-25/5	3,300	270	2×10^{-6}	2×10^{-3}
PFPE-Y-40/11	3,900	460	1×10^{-11}	5×10^{-7}
PFPE-Y-140/13	6,500	1400	5×10^{-13}	5×10^{-8}

PFPE-K DuPont, Krytox® lubricants

USA: Deepwater, NJ 08023; telephone, 800-424-7502, 609-540-3544

Europe (telephone)-32-3-543-1211

World Wide Web.: <http://www.lubricants.dupont.com>

PFPE-Y, Z Ausimont, Fomblin® lubricants

USA: 44 Whippany Rd, Morristown, NJ 07962; telephone, 201-292-6250

Europe: Via Principe Eugenio 1/5, Milan, Italy 39-02-62701

PFPE-D Daikin, Demnum® lubricants

Shinjuku-ku, Tokyo, Japan; telephone, 03-347-8346